

Entanglement in helium

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Using a configuration-interaction variational method, we accurately compute the reduced, single-electron von Neumann entropy for several low-energy, singlet and triplet eigenstates of helium atom. We estimate the amount of electron-electron orbital entanglement for such eigenstates and show that it decays with energy.

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I. INTRODUCTION

The role of entanglement as a resource in quantum communication and computation [1, 2] has stimulated many studies trying to unveil its fundamental aspects as well as to provide quantitative entanglement measures [3–5]. More recently, the role of entanglement attracts growing interest in systems relevant for chemistry and biology, for instance in light-harvesting complexes, governing the photosynthesis mechanism in proteins [6–11]. In such instances, due to the complexity of the involved systems, *ab initio* treatments are computationally prohibitive and one is forced to consider simplified (spin) models, with parameters introduced phenomenologically.

Besides computational problems for many-body quantum systems, one must address the problem of measuring entanglement for indistinguishable particles [12–16]. The main difficulty in quantifying entanglement is due to the symmetrization or antisymmetrization of the wave function for bosons or fermions. That is, to discriminate entanglement from correlations simply due to statistics of indistinguishable particles. In spite of this difficulty, bipartite entanglement has been investigated in a number of systems of physical interest, including the entanglement dynamics of electron-electron scattering in low-dimensional semiconductor systems [17] and the entanglement of low-energy eigenstates of helium atom [18].

To evaluate entanglement in helium, Ref. [18] used high-quality, state-of-the art Kinoshita-type wavefunctions [19], expressed in terms of Hylleraas coordinates [19–23], and then computed the purity of the reduced, one-electron density operator by means of a twelve-dimensional Monte Carlo numerical integration. In the present paper, we compute several low-energy states of helium by means of a simple configuration-interaction variational method. Our approach has several advantages. First of all, we do not need to evaluate

multidimensional integrals: the reduced density matrix is obtained by purely algebraic methods. The reduced density matrix can then be easily diagonalized and therefore we can access not only the linear entropy but also the von Neumann entropy. Finally, we express our variational, Slater-type basis, in terms of (radial and angular) single-particle coordinates, and therefore such Fock-state basis could be easily extended to many-body systems. Despite the above mentioned, still unsolved conceptual difficulties in the definition of entanglement for indistinguishable particles, we propose a way to evaluate the orbital entanglement for states close to Fock states. From such a measure we conclude that the amount of entanglement exhibited by helium eigenstates $|1s, ns; {}^1S\rangle$ and $|1s, ns; {}^3S\rangle$ drops with energy.

The paper is organized as follows. In Sec. II we define the measure used to estimate the entanglement of helium eigenstates. In Sec. III we shortly describe the variational method that we used to determine the low-energy reduced density operator ρ_1 . Our numerical results for entanglement of the helium atom are discussed in Sec. IV. Finally, our conclusions are drawn in Sec. V.

II. ENTANGLEMENT OF HELIUM EIGENSTATES

The non-relativistic Hamiltonian of the helium atom reads, in atomic units,

$$H = \frac{1}{2} \mathbf{p}_1^2 + \frac{1}{2} \mathbf{p}_2^2 - \frac{Z}{r_1} - \frac{Z}{r_2} + \frac{1}{r_{12}}, \quad (1)$$

where $Z = 2$ denotes the nuclear charge, \mathbf{p}_i the momentum of electron i ($i = 1, 2$), r_i its distance from the nucleus and r_{12} the inter-electronic separation.

Since we are neglecting the spin-orbit interaction, we can consider global wavefunctions Ξ factorized into the product of a coordinate wavefunction Ψ and a spin wavefunction χ :

$$\Xi_{\sigma_1, \sigma_2}(\mathbf{r}_1, \mathbf{r}_2) = \Psi(\mathbf{r}_1, \mathbf{r}_2) \chi_{\sigma_1 \sigma_2}. \quad (2)$$

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The overall state must be antisymmetric and therefore a measure [12] of the amount of entanglement $E(|\Xi\rangle)$ of the state Ξ has been proposed in terms of the von Neumann entropy of the reduced density operator $R_1 = \text{Tr}_2(|\Xi\rangle\langle\Xi|)$ of one particle, say particle 1, obtained after tracing the overall, two-body density operator over the other particle:

$$E(|\Xi\rangle) = S(R_1) - 1, \quad (3)$$

with the von Neumann entropy

$$S(R_1) = - \sum_i \Lambda_i \log_2 \Lambda_i, \quad (4)$$

where $\{\Lambda_i\}$ are the eigenvalues of R_1 .

However, with such definition a first problem arises. When considering the triplet subspace, spanned by the spin states $\chi_{\uparrow\uparrow}$, $\frac{1}{\sqrt{2}}(\chi_{\uparrow\downarrow} + \chi_{\downarrow\uparrow})$, and $\chi_{\downarrow\downarrow}$, it is clear that we should consider the case $\frac{1}{\sqrt{2}}(\chi_{\uparrow\downarrow} + \chi_{\downarrow\uparrow})$ separately from the cases $\chi_{\uparrow\uparrow}$ and $\chi_{\downarrow\downarrow}$. Indeed, $\frac{1}{\sqrt{2}}(\chi_{\uparrow\downarrow} + \chi_{\downarrow\uparrow})$ is a maximally entangled Bell state of the two spins while $\chi_{\uparrow\uparrow}$ and $\chi_{\downarrow\downarrow}$ are separable states. Therefore, the standard spectroscopic characterization in terms of triplet and singlet states is no longer useful for the purposes of computing entanglement and one should study separately the entanglement properties of the states composing the triplet. In this context, we would like to point out that, neglecting spin-spin interaction, the choice of the basis states spanning the triplet state is completely arbitrary and that the above discussed $\{\chi_{\uparrow\uparrow}, \frac{1}{\sqrt{2}}(\chi_{\uparrow\downarrow} + \chi_{\downarrow\uparrow}), \chi_{\downarrow\downarrow}\}$ is only one in between the infinite possible choices.

To avoid this ambiguity, in this paper we compute the entanglement for the orbital part Ψ only of the wavefunction. Since Ψ is antisymmetric for spins in the triplet subspace, we can measure the amount of entanglement $E(|\Psi\rangle)$ of Ψ as follows:

$$E(|\Psi\rangle) = S(\rho_1) - 1, \quad (5)$$

where

$$S(\rho_1) = - \sum_i \lambda_i \log_2 \lambda_i \quad (6)$$

is the von Neumann entropy of the reduced density operator $\rho_1 = \text{Tr}_2(|\Psi\rangle\langle\Psi|)$, and $\{\lambda_i\}$ are the eigenvalues of ρ_1 .

When the spin part of the wavefunction is in the singlet state $\chi_S = \frac{1}{\sqrt{2}}(\chi_{\uparrow\downarrow} - \chi_{\downarrow\uparrow})$, the orbital part is necessarily symmetric and this causes an additional, open problem in the quantification of entanglement. Indeed in this case the reduced von Neumann entropy alone is not sufficient to discriminate between entangled and separable states [15]. The core of the problem is the fact that we can have separable states with either $S(\rho_1) = 0$ or $S(\rho_1) = 1$. The first instance corresponds to basis states of the kind $\Psi_{ii}(\mathbf{r}_1, \mathbf{r}_2) = \phi_i(\mathbf{r}_1)\phi_i(\mathbf{r}_2)$, the second to basis states like $\Psi_{ij}(\mathbf{r}_1, \mathbf{r}_2) = \frac{1}{\sqrt{2}}[\phi_i(\mathbf{r}_1)\phi_j(\mathbf{r}_2) + \phi_j(\mathbf{r}_1)\phi_i(\mathbf{r}_2)]$,

with $i \neq j$. On the other hand, even the quantification of entanglement of the global, antisymmetric wavefunction by means of Eq. (3) poses a problem. Indeed, as the von Neumann entropy is additive for tensor products, for the state $\Xi = \Psi_{ii}\chi_S$ Eq. (3) gives $E(|\Xi\rangle) = 1$, while for the state $\Xi = \Psi_{ij}\chi_S$ ($i \neq j$) we have $E(|\Xi\rangle) = 2$. Even though measure (3) gives different results, the amount of entanglement in both cases is the same, since the orbital wavefunctions Ψ_{ii} and Ψ_{ij} are both separable: the reduced density matrices for these two states have different entropies only due to the symmetrization of the state Ψ_{ij} .

We will not address in this paper the unsolved problem of quantification of entanglement for a generic state Ψ . On the other hand, since from our calculations it turns out that for each low-energy helium eigenstate the reduced density operator for the orbital part is rather weakly perturbed with respect to one of the two above non-entangled cases, we expect that an approximate quantification of entanglement is provided by the distance between the von Neumann entropy $S(\rho_1)$ of ρ_1 and the von Neumann entropy $S(\rho_1^{(0)})$ ($S(\rho_1^{(0)}) = 0$ or $S(\rho_1^{(0)}) = 1$) of the reduced density operator $\rho_1^{(0)}$ for the corresponding non-interacting, non-entangled state:

$$E(|\Psi\rangle) = |S(\rho_1) - S(\rho_1^{(0)})|. \quad (7)$$

Note that for antisymmetric orbital wave functions this definition reduces to (5).

III. METHOD

We compute with high accuracy the lowest energy states of helium by means of a variational method, the configuration-interaction method (see, for instance, Ref. [24]). Orthonormal basis functions are provided by

$$\begin{aligned} \Phi_{n_1, l_1, m_1; n_2, l_2, m_2}(\mathbf{r}_1, \mathbf{r}_2) \\ = F_{n_1, l_1; n_2, l_2}(r_1, r_2) Y_{l_1 m_1}(\Omega_1) Y_{l_2 m_2}(\Omega_2), \end{aligned} \quad (8)$$

where Y_{lm} are spherical harmonics, with Ω_i solid angle for the particle i and the radial functions $F_{n_1, l_1; n_2, l_2}(r_1, r_2)$ are obtained after orthonormalizing the Slater-type orbitals

$$R_{nl}(r) = r^{n+l-1} \exp(-\xi_{n,l} r), \quad (9)$$

with $\xi_{n,l}$ variational parameters, and properly symmetrizing the products of the obtained one-particle radial wavefunctions $f_{nl}(r)$. That is, if the spin wavefunction is symmetric, F must be antisymmetric,

$$\begin{aligned} F_{n_1, l_1; n_2, l_2}(r_1, r_2) = \frac{1}{\sqrt{2}} [f_{n_1 l_1}(r_1) f_{n_2 l_2}(r_2) \\ - f_{n_2 l_2}(r_1) f_{n_1 l_1}(r_2)]; \end{aligned} \quad (10)$$

if the spin wavefunction is antisymmetric, F must be symmetric:

$$F_{n_1, l_1; n_2, l_2}(r_1, r_2) = \frac{1}{\sqrt{2}} [f_{n_1 l_1}(r_1) f_{n_2 l_2}(r_2) + f_{n_2 l_2}(r_1) f_{n_1 l_1}(r_2)] \quad (11)$$

if $(n_1, l_1) \neq (n_2, l_2)$,

$$F_{n_1, l_1; n_1, l_1}(r_1, r_2) = f_{n_1 l_1}(r_1) f_{n_1 l_1}(r_2) \quad (12)$$

otherwise.

We then compute the reduced (single-electron) density matrix

$$\rho_1(\mathbf{r}_1, \mathbf{r}'_1) = \int d\mathbf{r}_2 \Psi(\mathbf{r}_1, \mathbf{r}_2) \Psi^*(\mathbf{r}'_1, \mathbf{r}_2), \quad (13)$$

with

$$\Psi(\mathbf{r}_1, \mathbf{r}_2) = \sum_{I_1, I_2} c_{I_1, I_2} \Phi_{I_1, I_2}(\mathbf{r}_1, \mathbf{r}_2), \quad (14)$$

with the multi-indexes $I_1 \equiv (n_1, l_1, m_1)$ and $I_2 \equiv (n_2, l_2, m_2)$. Since the expansion is done over an orthonormal basis the reduced density matrix on that basis is simply given by a partial trace over the second particle of the overall density matrix: $(\rho_1)_{I_1, I'_1} = \sum_{I_2} \rho_{I_1, I_2; I'_1, I_2}$, where $\rho_{I_1, I_2; I'_1, I'_2} = c_{I_1, I_2} c_{I'_1, I'_2}^*$. We point out a major advantage of the configuration-interaction method: the reduced density matrix is obtained by purely algebraic methods, without numerical computation of the multi-dimensional integrals of Eq. (13). The reduced density matrix can then be easily diagonalized and in this paper we will study the entanglement properties of helium by means of the eigenvalues $\{\lambda_k\}$ of ρ_1 .

IV. NUMERICAL RESULTS

In the following, we will present data only for total orbital momentum quantum number $L = 0$, thus implying $l_1 = l_2 \equiv l$ and $m_1 = -m_2$.

We first discuss convergence of our method, as a function of the number $n_{\max}(l)$ of radial wavefunctions for a given l and as a function of the cut-off l_{\max} on l . For the low-energy states discussed below, we found that $l_{\max} = 2$ (S, P, and D shells) and $n_{\max} \approx 10 - 20$ (from $n_{\max} = 10$ for the ground state up to $n_{\max} = 20$ for the higher excited states reported below) are sufficient to reproduce helium eigenenergies with at least four significant digits (as deduced from comparison of our results with those of Refs. [19, 21–23]) and reduced von Neumann entropy $S(\rho_1)$, estimating at least two-three significant digits. To illustrate the convergence of our method, we provide in Table I the obtained values of $S(\rho_1)$ of the ground state of helium for different values of the cut-offs l_{\max} and n_{\max} (we take the same n_{\max} for all values of l).

	$l_{\max} = 0$	$l_{\max} = 1$	$l_{\max} = 2$	$l_{\max} = 3$
$n_{\max} = 5$	0.04131	0.07772	0.07844	0.07833
$n_{\max} = 6$	0.04133	0.07776	0.07848	0.07837
$n_{\max} = 10$	0.04134	0.07777	0.07849	0.07839
$n_{\max} = 11$	0.04134	0.07777	0.07849	0.07839

TABLE I. Reduced von Neumann entropy of the ground state of helium, computed with different cut-off values in the basis of Slater-type orbitals.

State	$S(\rho_1)$	$S_L(\rho_1)$
$ (1s)^2; ^1S\rangle$	0.0785	0.01606
$ 1s, 2s; ^1S\rangle$	0.991099	0.48871
$ 1s, 3s; ^1S\rangle$	0.998513	0.49724
$ 1s, 4s; ^1S\rangle$	0.999577	0.49892
$ 1s, 5s; ^1S\rangle$	0.999838	0.499465
$ 1s, 6s; ^1S\rangle$	0.999923	0.499665
$ 1s, 7s; ^1S\rangle$	0.999961	0.499777

TABLE II. Reduced von Neumann and linear entropies for the lowest energy singlet eigenstates of helium.

The reduced von Neumann entropy $S(\rho_1)$, as well as the linearized entropy $S_L(\rho_1) = 1 - \text{Tr}(\rho_1^2)$ often used in the literature, are shown in Table II and in Table III for several low-energy singlet and triplet eigenstates, respectively.

Since the obtained values of the von Neumann entropy are very close to those expected for Fock states, which are separable, the entanglement content is weak and can be estimated by means of Eq. (7). The obtained results are shown in Fig. 1 as a function of the state number n , for both singlet states $|1s, ns; ^1S\rangle$ and triplet states $|1s, ns; ^3S\rangle$. Note that data, with the exception of the ground state value of entanglement, are consistent with a power law decay of entanglement with n . From a power-law fit we obtained $E(n) = 0.19 n^{-4.41}$ for singlet states at $n \geq 2$ and $E(n) = 0.040 n^{-3.19}$ for triplet states. The same entanglement data are shown as a function of energy in Fig. 2. It can be clearly seen that the entanglement content drops with energy. This result is rather intuitive in that for states $|1s, ns; ^1S\rangle$ and $|1s, ns; ^3S\rangle$ the wave functions corresponding to the states $1s$ and ns are localized far apart for large n . Therefore, electron-

State	$S(\rho_1)$	$S_L(\rho_1)$
$ 1s, 2s; ^3S\rangle$	1.00494	0.500378
$ 1s, 3s; ^3S\rangle$	1.00114	0.5000736
$ 1s, 4s; ^3S\rangle$	1.000453	0.5000267
$ 1s, 5s; ^3S\rangle$	1.000229	0.5000127
$ 1s, 6s; ^3S\rangle$	1.000133	0.5000070
$ 1s, 7s; ^3S\rangle$	1.000091	0.5000047

TABLE III. Same as in Table II, but for the lowest energy triplet eigenstates of helium.

electron interactions become weaker (and entanglement smaller) when n increases. We note that, due to a different definition of entanglement, the energy-dependence obtained in our results contrasts the one obtained in Ref. [18].

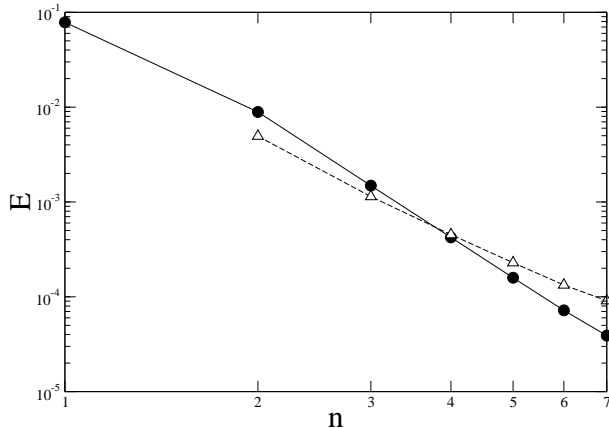


FIG. 1. Entanglement of the singlet states $|1s, ns; ^1S\rangle$ (circles) and of the triplet states $|1s, ns; ^3S\rangle$ (triangles).

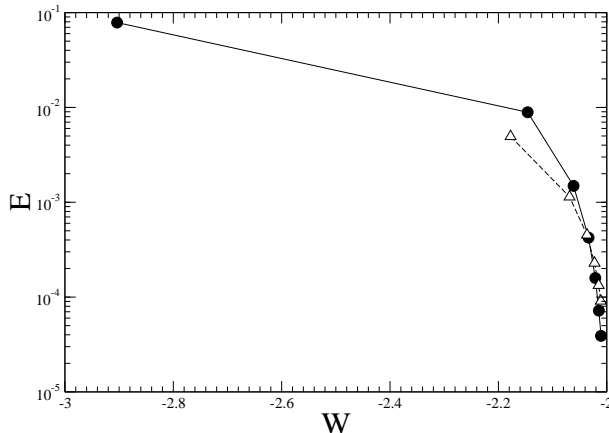


FIG. 2. Same as in Fig. 1, but with the entanglement of the helium eigenstates plotted as a function of their energy W (measured in hartrees).

V. CONCLUSIONS

In this paper, we have computed the reduced von Neumann entropy for several low-energy (singlet and triplet) eigenstates of helium. The von Neumann entropy has then been used to estimate the amount of entanglement of such states, showing that the entanglement of the states $|1s, ns; ^1S\rangle$ and $|1s, ns; ^3S\rangle$ decays with n , that is, with energy. This result is in agreement with the intuition, suggesting that when the electronic wavefunctions are localized far apart, electron-electron interactions are weak and therefore the entanglement is expected to be small. Our results can be seen as one of the first steps towards a “spectroscopy of entanglement” for atomic and molecular systems. While in this quest helium atom constitutes the simplest example, the variational scheme used in this paper may be extended to more complex systems, and the obtained numerical results could be used to test the validity of perturbative approaches or of simplified phenomenological models. Finally, we point out that, while our bipartite entanglement measure can be applied to wavefunctions close to separable Fock states, quantification of entanglement for generic states of indistinguishable particles remains an interesting open problem.

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